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New Nonlinear Polyurethane: Synthesis and Optical Properties

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The compound 3,4-di-(2′-hydroxyethoxy)-4-diphenyl-hydrazone-methyl was synthesized from the reaction of 3,4-dihydroxy-4-diphenyl-hyrazaone-methyl with 2-chloro-1-ethanol in a 1:2 mole ratio, and subsequent reaction with methylene-4,4′-diphenyldiisocyanate (MDI) to produce the new nonlinear polyurethane. The chemical structures of the resulting monomer and polymer were characterized by CHN analysis, FT-IR, 1H-NMR, and UV-Vis spectroscopy. The nonlinear optical properties of new polyurethane have been studied via second harmonic generation (SHG). The values of electro-optic coefficient $d_{33}$ and $d_{31}$ of the poled polyurethane film were $6.62 \times 10^{-9}$ and $3.05 \times 10^{-8}$ esu, respectively.

Thermal behavior of this polyurethane was studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

Keywords Nonlinear; Optical properties; Polyurethane; Second harmonic generation; Synthesis

INTRODUCTION

Many investigations based on non-linear optical (NLO) properties of organic polymers have been increased considerably in recent years[1], due to they possess many advantages such as mechanical endurance, lightweight, chemical resistance, and good processability to form optical devices[2–5]. Polymeric and organic second-order NLO materials have drawn much interest in the past years due to their potential application in photonics[6]. Hence, in the development of NLO polymers for electro-optic device applications[7], the stabilization of electrically induced dipole alignment is an important consideration. One of the current challenges is to design novel NLO polymers having optimized properties. Two approaches to minimize randomization either using the cross-linking method[8,9] or utilize high $T_g$ polymers[10,11].

There are tremendous challenges in designing and synthesis of polymers of large NLO effects. Polyurethane containing the chromophoric main chain[12–14] or side chain[15,16] was prepared and characterized. Main chain polymers have good thermal stability of dipole alignments, but have a poor solubility in organic solvents, and this intractability makes it impossible to fabricate stable noncentrosymmetric films. Side-chain polymer systems have the advantages such as homogeneity and high-level of NLO chromophore density relative to the host-guest systems, but they often suffer from poor stability of dipole alignments at high temperature. Ju-Yeon Lee et al.[17,18] have reported different types of NLOs such as $Y$ and $T$-type of polyurethanes based on -C=C- as chromophore in the backbone of these polymers and exhibited good properties.

In this work, we prepared novel NLO polyurethane containing azomethine (-CH=N-) group in the main chain as the chromophore because this group has a large dipole moment in addition it is easy to be synthesized. Furthermore, we expect this new NLO polyurethane has side chains and main chains, which possesses good solubility and stabilization of dipole alignment.

EXPERIMENTAL

Materials

Methylene-4,4′-diphenyldiisocyanate (MDI) was purchased from Aldrich Co. (USA) and purified by distillation under reduced pressure. The chemicals 1,1-diphenylhydrazine hydrochloride, 3,4-dihydroxybenzaldehyde, sodium acetate trihydrate, anhydrous sodium carbonate, magnesium sulphate (MgSO₄) and 2-chloro-1-ethanol were purchased from Fluka Co.(Germany) and used as received. Ethyl acetate, n-hexane, chloroform, dimethyl-sulphoxide (DMSO), 1-butanol, and ethanol were all supplied by Systerm (Malaysia). N,N-dimethylformamide (DMF) was also purchased from Fluka Co. (Germany) and purified by drying with calcium hydride, followed by distillation under reduced pressure.

Measurements

FT-IR spectrophotometer measured in Perkin–Elmer 2000 using KBr pellets for monomers and polymer ranged from 4000 to 400 cm$^{-1}$. 1H–NMR spectra were obtained using Bruker 400 MHz NMR spectrometer in DMSO–d$_6$ as the solvent and Tetramethylsilane (TMS) as the internal reference. The UV–Vis spectrum of the polyurethane was
recorded with a HITHASHI U–2000 spectrophotometer. Thermogravimetric analysis (TGA) was carried out in nitrogen atmosphere with Perkin–Elmer TGA7 series at 10°C min⁻¹.

Differential scanning calorimetry (DSC) measurements were carried out with a Perkin–Elmer DSC7 series at heating rate of 10°C min⁻¹ in nitrogen. Inherent viscosity of polyurethane solution (0.2 dL/g in DMSO) was determined at 30°C in an Ubbelohde viscometer. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the polyurethane was conducted by gel permeation chromatography (GPC). The refractive index of the synthesized NLO polyurethane was measured by optical transmission technique[19].

Studies of the alignments of the NLO-chromophores of the polyurethane were carried out by the corona-poling method. The temperature was raised to 152°C, 6.5 kV of corona voltage was applied and kept at 152°C for 30 min. Second harmonic generation (SHG) measurements were carried out immediately after poling. A Q-switched Nd : YAG laser (λ = 1064 nm), with a pulse width of 10 ns and repetition rate of 10 Hz, was used as the fundamental light source and Y-cut quartz was used as reference. SHG coefficients (d_22) were derived from the analysis of measured Maker-fringes[20,21].

Preparation of 3,4-di-(2-hydroxyethoxy)-4-diphenylhydrazonomethyl (I)

To a magnetically stirred solution of 1.4 g (6.35 mmol) of 1,1-diphenylhydrazine hydrochloride in 40 ml of ethanol was added 1.29 g (9.54 mmol) of sodium acetate trihydrate at room temperature. Then a solution of 3,4-dihydroxybenzaldehyde (1.2 g, 6.36 mmol) in 40 ml ethanol was added dropwise for 30 min. After stirring for 4 h, ethanol was removed under reduced pressure and the residue was poured into water. The product was extracted with chloroform, washed with plenty of brine and distilled water, and dried under vacuum. The percent yield was 94%, FT-IR (KBr disc): 3412 cm⁻¹ (OH stretch), 1613 cm⁻¹ (C=O stretch), 1513 cm⁻¹ (C=C). Elemental analysis: Found: C, 70.66; H, 6.53; N, 8.72. Calc.: C, 70.40; H, 6.12; N, 7.14.

Preparation of Polyurethane (III)

Methylene-4,4'-diphenyldiisocyanate (MDI) (0.01 mol) in 30 ml of N,N-dimethylformamide (DMF) was added to a mixture of 3,4-di-(2-hydroxyethoxy)-4-diphenylhydrazonomethyl (0.01 mol) (II) in DMF at 60°C for 1 h. Subsequently the temperature of the reaction mixture was increased to 120°C and continued stirring under nitrogen overnight. The polyurethane (III) prepared was precipitated in distilled water, filtered, and washed several times with distilled water, then with methanol and dried for 24 h in a vacuum oven at 80°C. The percent yield was 89%, FT-IR (KBr disc): 3327 cm⁻¹ (NH stretch), 1707 cm⁻¹ (C=O stretch), 1513 cm⁻¹ (C=C). Elemental analysis: Found: C, 70.19; H, 5.33; N, 8.40. Calc.: C, 71.02; H, 5.29; N, 8.72.

RESULTS AND DISCUSSION

NLO Polyurethane Synthesis

NLO polyurethane was prepared by the addition reaction between monomer (II) and methylene-4,4’-diphenyldiisocyanate (MDI). The chemical structure of the resulting NLO polyurethane (Scheme 1) was confirmed by FT-IR, ¹H-NMR spectra and elemental analysis (CHN). The characteristic IR absorption band of urethane was found at 1707 cm⁻¹ due to carbonyl C=O, at 3327 cm⁻¹ due to N-H stretching, other absorption bands due to the aromatic ring at 1599, 1513 cm⁻¹, and azomethine group –CH=N– at 1654 cm⁻¹ as shown in Figure 1. The ¹H-NMR spectrum of the polyurethane (III) is shown in Figure 2. Singlet peaks at 9.85, 8.45, and 3.86 ppm are due to the protons in urethane NH-COO linkages, azomethine (–CH=N–) and methylene (Ph-CH₂–Ph) group, respectively. The spectrum shows two characteristic triplet peaks at 4.46 ppm due to the protons in the methylene (Ph–O–CH₂) group and at 3.78 ppm due to the (proton (–CH₂–O–CO), thus indicating the formation of urethane linkage. Multiplet peaks at 6.25–7.88 ppm are assigned to the aromatic protons. The molecular weight was determined by GPC using polystyrene as the standard and THF as an eluent. The number average molecular weight (M_n) of polyurethane (III) determined by GPC
was 11,800 ($M_w/M_n = 1.6$). The NLO polyurethane (III) was well soluble in common solvents such as DMAc, trichloroacetic acid, DMF and DMSO while insoluble in methanol and diethyl ether. The inherent viscosity was 0.36 dL/g (measured in DMSO at 30°C, $c = 0.2$ g dL$^{-1}$).

**Thermal and Nonlinear Optical Properties of Polyurethane III**

Thermal behavior of the NLO polyurethane (III) was analyzed based on thermogram obtained from TGA in Figure 3 at constant heating rate of 10°C min$^{-1}$ under nitrogen atmosphere, and differential scanning calorimetry (DSC). From the TGA curve, the initial decomposition temperature was defined as the temperature of 10% weight loss. The decomposition of polyurethane took place in one step at 340°C higher than research reported$^{[18]}$, which started degradation at 260°C.

From the DSC trace, glass transition temperatures ($T_g$) of polyurethane was found at 142°C. The TGA and DSC studies showed that the decomposition temperature of the NLO polyurethane (III) was higher than the corresponding $T_g$. This indicates that high-temperature poling for short term is feasible without damaging the NLO chromophore.

The NLO property of polyurethane (III) was studied by the SHG method. To induce noncentrosymmetric polar order, the spin-coated polyurethane film was corona-poled. As the temperature was raised to 152°C, 6.5 kV of corona voltage was applied and kept at 152°C for 30 min. The UV-Vis absorption spectrum of the polyurethane before and after the poling was recorded. After the electric poling,
the dipole moment of the NLO-chromophore was aligned and UV-Vis spectrum of the NLO polyurethane exhibited blue shift. From the absorbance change, the order parameter of the poled film could be estimated, which is related to the poling efficiency.

The estimated order parameter value, \( \Phi \), was found 0.18 for polyurethane (III). \( \Phi = 1 - A_1 / A_0 \), \( A_0 \) and \( A_1 \) are the absorbance’s of the polyurethane film before and after poling, respectively. The refractive index of the NLO polyurethane was measured by the optical transmission technique\(^{[19]} \). SHG measurement was performed at a fundamental wavelength of 1064 nm using a mode locked Nd-YAG laser. In order to determine the microscopic second-order susceptibility of the polyurethane (III), the angular SHG dependence was recorded.

The SHG value was compared with those obtained from a Y-cut quartz plate. To calculate the \( d_{31} \) and \( d_{33} \) values, both s-polarized and p-polarized IR laser were directed to the sample and recorded. A nonlinear optical property of the polyurethane (III) is summarized in Table 1. To investigate the real time NLO decay of the SHG signal of the poled NLO polyurethane film as a function of temperature, in situ SHG measurement (Figure 4) was performed at a heating rate of 10°C/min from 30°C to 240°C. The NLO polyurethane (III) film exhibited thermal stability even at 10°C higher than \( T_g \) and no significant SHG decay was observed below 152°C.

Stabilization of dipole alignment is a characteristic of main chain of NLO polymer. The exceptionally high thermal stability of second harmonic generation of NLO polyurethane (III) is due to the stabilization of dipole alignment of NLO chromophore, which stems from the partial main chain character of the polymer structure. Thus, we obtained new NLO polyurethane having both of the merits of main chain and side chain NLO polymer; stabilization of dipole alignment and good solubility. This makes NLO polyurethane III an interesting material for the realization of electro-optic device applications.

**TABLE 1**

<table>
<thead>
<tr>
<th>Polyurethane</th>
<th>( d_{31} ) (emu)</th>
<th>( d_{33} ) (emu)</th>
<th>( \Phi ) *</th>
<th>( \lambda_{max} ) (nm)</th>
<th>Film thickness (µm)</th>
<th>Refractive Index</th>
<th>ms</th>
<th>np</th>
</tr>
</thead>
<tbody>
<tr>
<td>III</td>
<td>( 6.62 \times 10^{-4} )</td>
<td>( 3.05 \times 10^{-4} )</td>
<td>0.18</td>
<td>398</td>
<td>0.45</td>
<td>1.61</td>
<td>1.74</td>
<td></td>
</tr>
</tbody>
</table>

\*Order parameter \( \Phi = 1 - A_1 / A_0 \), \( A_0 \) and \( A_1 \) are the absorbance’s of the NLO polyurethane film before and after corona poling, respectively.

**CONCLUSION**

New NLO polyurethane was successfully synthesized and characterized by CHN elemental analysis, FT-IR, \(^1\)H-NMR and UV-Vis techniques. The nonlinear polyurethane (III) has good solubility in DMAC, trichloroacetic acid, DMF and DMSO. The second harmonic generation (SHG) of the NLO polyurethane showed it exhibit high thermal stability of second harmonic generation due to the stabilization of dipole alignment of NLO chromophore, which stems from the partial main chain character of the polymer structure.

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